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**(19) (CA) APPLICATION FOR CANADIAN PATENT (12)**

(54) Process for Producing Lower Alkyl Fatty Acid Esters

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Notice: This application is as filed and may therefore contain an incomplete specification.



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## ABSTRACT OF THE DISCLOSURE

The present invention provides improved processes for methanolysis and ethanolysis of fatty acid glycerides such as those found in naturally occurring fats and oils derived from plants and animals. The processes comprise solubilizing an oil or fat in methanol or ethanol by the addition of a cosolvent in order to form a one phase reaction mixture, and adding an esterification catalyst. The processes proceed quickly, usually in less than 20 minutes, at ambient temperatures, atmospheric pressure, and without agitation. The cosolvent increases the rate of the reaction by making the oil soluble in the methanol, thus increasing contact of the reactants. The lower alkyl fatty acid monoesters produced by the processes can be used as biofuels and are suitable as diesel fuel replacements or additives.

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PROCESS FOR PRODUCING LOWER  
ALKYL FATTY ACID ESTERS

FIELD OF THE INVENTION

This invention relates to a process for converting fats and oils to lower alkyl fatty acid esters useful as biofuels.

BACKGROUND OF THE INVENTION

Much attention has recently been directed to the use of "biofuels" as replacements for hydrocarbon fuels such as diesel fuel. Biofuels may be defined as fuels derived from renewable resources such as biomass materials.

Naturally occurring fats and oils from plants and animals have shown promise as possible sources of biofuels. Fats are solid at room temperature and are generally derived from animals. Oils are liquid at room temperature and are generally derived from plants.

Oils and fats can generally be described as fatty acid esters of glycerol, also known as fatty acid glycerides. The major components of an oil or fat are the fatty acid triglycerides, in which three long chain fatty acid moieties are joined to one glycerol moiety by ester linkages.

Unmodified vegetable oils have been tested in diesel engines and can be used as diesel fuel replacements or additives on a relatively short term basis. However, the relatively high viscosity of vegetable oils causes poor atomization, ignition and combustion, resulting in carbon deposits on injection nozzles, chamber walls and piston heads, oil ring sticking and thickening of the lubricating oil. Therefore, unmodified vegetable oils are unsuitable as diesel fuel replacements or additives on a long term basis.

The high viscosity of vegetable oils results from their relatively high molar masses (approximately 870

Daltons for soybean oil). Transesterification is one process by which the molar mass and the viscosity of an oil can be lowered significantly. Other known processes include thermal or catalytic cracking and electrolysis.

In a typical process for transesterification of fats and oils, the glycerol moiety of each triglyceride is replaced by three molecules of a lower molecular weight alcohol to yield three fatty acid monoesters, the molar masses of which are approximately 1/3 that of the triglyceride.

Although a wide range of alcohols can be used in the transesterification of fats and oils, only methanol and ethanol are practically useful on an industrial scale due to their low cost.

It has been found that methyl and ethyl fatty acid esters perform as well as regular diesel fuel comprising mainly unbranched paraffins, and perhaps better. In fact, methyl and ethyl esters are superior in many ways to conventional diesel fuel because they have higher flash points, lower toxicity, produce no explosive air/fuel vapours, produce no net carbon dioxide, sulphur or aromatics, produce fewer particulate emissions, are derived from renewable resources, and are biodegradable. Further, diesel engines perform well with fatty acid esters with little or no engine modification.

Most known transesterification processes for producing biofuel are slow and require relatively harsh reaction conditions, such as vigorous agitation, elevated temperatures, and sometimes elevated pressures, to drive the reaction to completion. Even under such conditions, methanolysis typically requires a reaction time of about one to four hours. Ethanolysis is also slow, but not as slow as methanolysis.

In one known methanolysis process discussed in Freedman et al, JAOCS, Vol. 61, no. 10 (October 1984), it was found that hydroxide ion catalyzed methanolysis of

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soybean oil was complete after 1 hour at 45°C and 60°C, and complete after 4 hours at 32°C, stirring being used to mix the reactants.

Freedman et al also report that ethanolysis of soybean oil carried out at 75°C with 0.5% NaOCH<sub>3</sub> was substantially complete after about 30 to 60 minutes, with stirring.

In another known process, methanolysis is carried out at a temperature of about 95°C (the boiling point of methanol is 64.5°C) and a pressure of about 50 psi.

The inherent dangers in operating transesterification processes on an industrial scale at or above the boiling points of volatile alcohols such as methanol and ethanol are obvious. Any leak in the reaction vessels would result in the release of highly explosive methanol and ethanol vapours.

Further, agitation of the reaction mixture may result in the formation of emulsions which hinder separation of glycerol from the product mixture. This problem is particularly serious when unrefined oils and fats, containing relatively high amounts of free fatty acids, are used in a base catalyzed process due to the formation of soaps.

Therefore, the disadvantage exists that no process has been proposed which substantially increases the rates of methanolysis and ethanolysis of fatty acid glycerides while simultaneously utilizing milder reaction conditions.

#### SUMMARY OF THE INVENTION

To at least partially overcome these disadvantages, the present invention provides improved methanolysis and ethanolysis processes, suitable for use on laboratory and industrial scales, for the production of high yields of methyl and ethyl fatty acid esters from fats and oils under mild reaction conditions.

The reactions are typically substantially complete in less than about 20 minutes, and proceed at atmospheric pressure, substantially without agitation, and at temperatures lower than the boiling point of the alcohol. A clean, fast separation of glycerol is achieved substantially without the formation of emulsions.

The inventor has discovered that the slow rates of methanolysis and ethanolysis are at least partially caused by the low solubilities of oils and fats in methanol and ethanol. Generally, fats and oils are not completely miscible with methanol and ethanol. Therefore, methanol and ethanol typically form two phase systems with fats and oils.

The inventor discovered that the rates of methanolysis and ethanolysis under mild conditions can be substantially increased by making oils and fats completely miscible in methanol and ethanol, so that a one phase system is produced.

The inventor found that one phase methanol/oil and ethanol/oil systems can be produced by the addition of a cosolvent to the reaction mixture. The most effective cosolvents are cyclic ethers, primarily because they form hydrogen bonds with polar compounds such as water and alcohols, contain sufficient non-polar hydrocarbon groups to dissolve high molecular weight oils and fats, and are chemically inert.

The inventor found that the addition of at least an amount of cosolvent sufficient to produce a one phase reaction mixture increases the rates of methanolysis and ethanolysis by as much as 15 times under mild conditions, the transesterification being substantially complete in less than about 20 minutes. Further, the glycerol separation may be 4 to 5 times faster than in reaction mixtures containing no cosolvent.

One object of the present invention is to provide improved processes for the production of biofuels.

Another object of the present invention is to provide processes for methanolysis and ethanolysis of fats and oils which proceed quickly under mild reaction conditions.

In known methanolysis and ethanolysis processes where a two phase system is produced, the reaction between the alcohol and the triglyceride takes place in the alcohol phase in the presence of the catalyst, which is soluble in the alcohol. However, due to the low solubility of most oils and fats in methanol and ethanol, the alcohol phase contains very little triglyceride available for reaction. Further, because it may take a long time to reach saturation levels, there is a significant time lag between the start of the reaction and the appearance of the first lower alkyl fatty acid esters.

For example, soybean oil is only slightly soluble in methanol, the solubility being 5.7 g/L at 30°C and 7.5 g/L at 40°C with vigorous stirring. Further, a significant amount of time is required to reach saturation levels. This low solubility can be explained by the fact that methanol is a fairly polar solvent, which does not have a high affinity for molecules such as fats and oils which typically have long, non-polar hydrocarbon chains.

In contrast to known methanolysis and ethanolysis processes, the processes of the present invention proceed quickly at atmospheric pressure and at temperatures below the boiling point of the alcohol, preferably ambient temperatures. Further, stirring of the reaction mixture is substantially not required since the alcohol and the fat or oil are both dissolved in a single phase.

The processes of the present invention comprise combining methanol or ethanol; a source of fatty acid glycerides such as fats, oils and mixtures thereof; a cosolvent; and an esterification catalyst.

Stoichiometry requires three moles of alcohol for each mole of fatty acid triglyceride. The reaction proceeds

in a stepwise fashion, through diglyceride and monoglyceride intermediates. However, because each step of the reaction is an equilibrium, an excess of alcohol is required to drive it to completion. The molar ratio of alcohol to the source of fatty acid is preferably at least about 4.5:1, and more preferably at least about 6:1.

The catalyst is preferably a basic esterification catalyst and is added in a catalytically effective amount, preferably not greater than about 2% by weight of the oil or fat. Alkoxides and hydroxides are preferred catalysts.

The fats and oils may be either refined or unrefined, and may be either virgin or recycled. Unrefined oils typically have higher amounts of free fatty acids than refined oils. The unrefined oils are preferably degummed and filtered. Further, when using unrefined oils, an additional amount of catalyst must be added sufficient to neutralize the free fatty acids.

A cosolvent is added in at least an amount sufficient to dissolve the source of fatty acid glycerides in the alcohol phase. Cyclic ethers such as tetrahydrofuran (THF) and 1,4-dioxane are the preferred cosolvents, with THF being the most preferred cosolvent, particularly for the methanolysis process.

A preferred batch process according to the present invention comprises dissolving the catalyst in the alcohol, dissolving the triglyceride in the cosolvent, and mixing the two solutions.

A preferred continuous process comprises dissolving the catalyst in an alcohol/cosolvent mixture and adding this solution to the triglyceride.

As the reaction proceeds, the reaction mixture separates into two layers, a lower glycerol layer and an upper layer containing ester products, excess alcohol, and cosolvent. The inventor has found that rapid separation of glycerol results in a faster reaction and also produces

higher yields by driving the reaction to completion.

The lower glycerol layer is preferably removed by gravitation or centrifugation. The ester product is isolated from the upper layer by removal of the cosolvent and excess alcohol, preferably by distillation at atmospheric or reduced pressure.

Surprisingly, the inventor has found that the addition of a cosolvent to the reaction mixture does not inhibit the phase separation of glycerol, which has been found to separate approximately four to five times faster than in processes which do not utilize a cosolvent. Further, separation of glycerol is achieved substantially without the formation of emulsions, even when using fats and oils not having been refined to remove free fatty acids.

The yield of esters is typically 80 to 98% of theoretical with refined oils and about 65 to 85% with unrefined oils.

The inventor has found that the addition of the cosolvent increases the volume of the reaction mixture only moderately, typically less than about 25%. This moderate increase in volume is accompanied by a dramatic increase in reaction rate, which is up to 15 times faster. Therefore, existing ester plants could increase output significantly without a substantial increase in capacity. Further, the mild reaction conditions of the inventive processes require relatively simple plant equipment.

Accordingly, in one aspect the present invention provides a process for the production of lower alkyl esters of fatty acids, comprising: reacting a source of fatty acid glycerides with an alcohol in the presence of an esterification catalyst and a cosolvent, wherein: (a) the source of fatty acid glycerides is selected from the group comprising fats and oils derived from plants and animals; (b) the alcohol is selected from the group comprising methanol, ethanol and mixtures thereof in an amount sufficient to substantially completely convert the source of

fatty acid glycerides to lower alkyl fatty acid monoesters; (c) the esterification catalyst is present in an amount sufficient to catalyze the process; and (d) the cosolvent is present in at least an amount sufficient to solubilize the source of fatty acid glycerides in the alcohol at a temperature below the boiling point of the alcohol; the process being carried out at a temperature below the boiling point of the alcohol for a time sufficient to allow the source of fatty acids to be substantially completely converted to lower alkyl fatty acid esters; and after completion of the reaction, separating the lower alkyl fatty acid esters from the reaction mixture.

In another aspect the present invention provides a process for the production of methyl esters of fatty acids, comprising reacting a source of fatty acid glycerides with an alcohol in the presence of an esterification catalyst and a cosolvent wherein: (a) the source of fatty acid glycerides is selected from the group comprising fats and oils derived from animals and plants having an acid value less than about 1; (b) the alcohol is methanol in a molar ratio of about 6:1 to the source of fatty acid glycerides; (c) the catalyst is selected from the group comprising sodium methoxide and sodium hydroxide and is present in an amount of about 0.4 to 2% by weight of fatty acid glyceride; and (d) the cosolvent is tetrahydrofuran and is present in at least an amount sufficient to solubilize the source of fatty acid glycerides in methanol; the process being carried out at about 15 to 30°C and reacted without agitation for a time sufficient to allow the source of fatty acid glycerides to be substantially completely converted to methyl esters of fatty acids; and separating the methyl fatty acid esters from the reaction mixture.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred processes for methanolysis and ethanolysis of fats and oils according to the present invention are now described.

The alcohol used in the transesterification processes of the present invention is preferably either methanol or ethanol, with methanol being most preferred. Methanol boils at 64.5°C and ethanol boils at 78.3°C. The alcohol is preferably substantially anhydrous, preferably containing less than about 0.5% water by weight.

Because transesterification is an equilibrium reaction, an excess of alcohol is required to drive the reaction to completion and to achieve a high yield. Theoretically, three moles of alcohol are required to react with each mole of triglyceride. However, it is preferred that the mole ratio of alcohol to the source of fatty acid glyceride be at least about 4.5:1, more preferably at least about 4.8:1 and most preferably at least about 6:1. The best balance between yield and economy is achieved at a ratio of about 6:1. At this ratio, yields as high as 98% can be achieved.

A wide range of oils and fats derived from animals and plants can be used as the source of fatty acid glycerides, including beef tallow, coconut oil, corn oil, cottonseed oil, lard, olive oil, palm oil, palm kernel oil, peanut oil, soybean oil, linseed oil, tung oil, sunflower oil, safflower oil, canola oil, sesame oil, babassu oil, perilla oil, oiticica oil, fish oils, menhaden oil, castor oil, rapeseed oil, Chinese tallow tree oil, physic nut oil, Cuphea seed oil, microalgal oils, bacterial oils and fungal oils.

Typically, the fats and oils each contain a mixture of several different saturated and/or unsaturated fatty acids in the form of glycerides. For example, soybean oil typically contains about 7 to 11 % C<sub>16</sub> saturated fatty acids, 2 to 5 % C<sub>18</sub> saturated fatty acids, 1 to 3 % higher than C<sub>18</sub> saturated fatty acids, 22 to 34 % monounsaturated C<sub>18</sub> fatty acids, 50 to 60 % di-unsaturated C<sub>18</sub> fatty acids and 2 to 10 % tri-unsaturated C<sub>18</sub> fatty acids.

The most preferred sources of fatty acids are

soybean oil, palm oil, palm kernel oil, coconut oil and canola oil because they are inexpensive and available in large quantities. However, the other fats and oils listed above are also suitable in the production of biofuel.

The oils and fats may be either refined, partially refined or unrefined. Unrefined oils and fats and some partially refined oils and fats typically comprise mixtures of fatty acid triglycerides as the major component, with free fatty acids and fatty acid mono- and diglycerides as minor components. Refined oils and some partially refined oils have low levels of free fatty acids, most of the free fatty acids being removed during refining.

Refined oils and fats, also referred to as "edible grade", are typically produced by degumming, alkali-refining to remove free fatty acids, bleaching, filtering and deodorizing. Partially refined oils are produced by degumming, filtering and optionally alkali-refining.

The oils and fats may be "virgin" products or may be recycled waste oils and fats such as used frying oils.

Preferred in the processes of the present invention are partially refined fats and oils, those having been alkali-refined for removal of free fatty acids being most preferred. The bleaching and deodorizing steps used to produce edible grade oils and fats are not necessary to produce biofuels. The most preferred oils and fats for use in the present invention have an acid value less than about 1 (less than about 0.5 % by weight free fatty acid) and are substantially anhydrous, preferably containing less than about 0.5 % water.

The cosolvent is added in at least an amount sufficient to form a one phase solution of the alcohol, source of fatty acid glyceride and cosolvent. The cosolvent is preferably completely miscible with both the alcohol and the source of fatty acid glyceride. Preferred cosolvents are cyclic ethers, which have a hydrophilic oxygen atom capable of forming hydrogen bonds with water and alcohols,

and a hydrophobic hydrocarbon portion capable of solubilizing many organic compounds. Larger amounts of cosolvent can be added than are required to solubilize the oil or fat with equally satisfactory results.

Preferably, the cosolvent has a boiling point of less than about 120°C to facilitate solvent removal after the reaction is complete. More preferably, the cosolvent has a boiling point similar to that of the alcohol. Preferred cosolvents are cyclic ethers such as THF and 1,4-dioxane.

The cosolvent is preferably anhydrous, preferably containing less than 0.5% by weight water.

The most preferred cosolvent for the methanolysis and ethanolysis reaction is THF. THF is particularly preferred for the methanolysis partly because its boiling point of 67°C is only slightly higher than that of methanol, thus allowing the unreacted methanol and THF to be easily co-distilled and recycled at the end of the reaction. Further, THF is cheaper than dioxane, inert, non-toxic and is itself of biomass origin.

At a temperature of about 15 to 30°C, the cosolvent is preferably present in at least an amount necessary to achieve a one phase system of alcohol, source of fatty acid glyceride and cosolvent. The amount of cosolvent needed depends on the particular source of fatty acid glyceride, alcohol and cosolvent being used.

In the case of soybean oil methanolysis, a volumetric ratio of about 1.25:1 THF to methanol is necessary to achieve a one phase alcohol/source of fatty acid glyceride/cosolvent reaction mixture at about 15 to 30°C. For ethanolysis of soybean oil, the minimum ratio of THF to ethanol is only about 0.25:1. When 1,4-dioxane is used in soybean oil methanolysis, the minimum dioxane to methanol ratio is about 1.5:1. For coconut oil and canola oil, the ratios are about 0.57 and 1.25, respectively, using THF as the cosolvent.

When the amount of cosolvent added is the minimum amount to achieve miscibility, some stirring of the reaction mixture may be required to obtain a one phase system. To avoid the need for stirring, an excess of cosolvent may be added to achieve instant miscibility. In the case of THF, a 1.6:1 volume ratio of the THF:methanol achieves instant miscibility. Generally, about a 20 to 30% excess of cosolvent is required to achieve instantaneous miscibility. This dilution of the reaction mixture has a negligible effect on the reaction rate.

Surprisingly, in a methanolysis reaction mixture having a 6:1 molar ratio of methanol:soybean oil, the addition of 1.25 equivalents by volume of THF to volume of methanol increases the reaction mixture volume by only 22%. This is because the soybean oil accounts for a relatively large proportion of the total volume.

The reaction is preferably carried out below the boiling point of the alcohol, i.e. preferably less than about 65°C for the methanolysis and preferably less than about 78°C for the ethanolysis. More preferably the methanolysis and ethanolysis are carried out at temperatures less than about 60°C, more preferably in the range from about 10 to about 40°C and most preferably in the range from about 15 to about 30°C. Further, the reaction is preferably carried out without substantial agitation of the reaction mixture.

The esterification catalyst is preferably a basic esterification catalyst. Basic esterification catalysts are preferred because the acid-catalyzed esterification reaction is slower and requires a higher temperature than the corresponding base-catalyzed reaction. Further, acid is corrosive and therefore requires the use of corrosion resistant reaction vessels.

Preferred basic catalysts include alkoxides such as methoxide, ethoxide, propoxide and butoxide; and hydroxides. More preferred basic catalysts are sodium

methoxide, potassium hydroxide and sodium hydroxide.

For achieving the highest possible yields, sodium methoxide is the most preferred catalyst. However, sodium hydroxide is the most preferred catalyst from a standpoint of convenience and ease of handling.

The amount of esterification catalyst added to catalyze the reaction is preferably not greater than about 2% by weight of the source of fatty acid glycerides, with about 0.4% to about 1.5% being more preferred. The amount of alkoxide is most preferably about 0.5% and the most preferred amount of hydroxide is about 0.5 to about 1%.

Free fatty acids are particularly troublesome components of fats and oils, particularly where the transesterification reaction is base catalyzed. Free fatty acids are neutralized to form soaps, thus consuming the basic catalyst. Therefore, additional catalyst is preferably added to compensate for the presence of free fatty acids. When using oils and fats which have not been refined for removal of free fatty acids, the amount of basic catalyst sufficient to catalyze the reaction includes an amount which neutralizes the free fatty acids. The preferred amounts of catalyst taught above do not include an amount to neutralize free fatty acids.

When using sodium methoxide as the catalyst, the only products of any significance are lower alkyl fatty acid esters, glycerol and small amounts of mono- and diglycerides.

When using sodium hydroxide, hydroxide ion can attack the lower alkyl fatty acid esters and glycerides to form sodium salts of carboxylic acids, i.e. soaps. The amount of sodium hydroxide is preferably minimized to reduce the amount of this side reaction. The inventor has found that in the methanolysis of refined soybean oil, the yields attained when using 0.5%, 1.0% and 2.0% sodium hydroxide are 95.4%, 92.7% and 85.4% respectively. Therefore, the amount of sodium hydroxide is most preferably limited to 0.5%, not

including amounts required to neutralize free fatty acids.

Further, excessive formation of soaps, either through the use of fats or oils having significant amounts of free fatty acids, or through the hydroxide side reaction, can result in the formation of emulsions. This slows the glycerol separation, resulting in lower yields and a slower reaction.

By using refined or partially refined oils having small amounts of free fatty acids, and by minimizing the hydroxide side reaction, the reaction is faster and higher yields are achieved. The fact that the alcohol, catalyst and source of triglyceride are dissolved in a single phase permits the use of small amounts of hydroxide catalyst, thus reducing the side reaction.

Basic catalysts are preferably substantially moisture free, preferably containing less than about 3% water, and are preferably stored under substantially anhydrous conditions. Prolonged contact of basic catalysts with air is also preferably avoided since water and carbon dioxide diminish effectiveness of the catalyst.

The basic catalyst is preferably added to the reaction mixture in the form of a solution, either in alcohol or in an alcohol/cosolvent mixture. Heat and stirring may be necessary to dissolve the catalyst. The alcoholic solution of basic catalyst is preferably added quickly to the reaction mixture, the addition time being dependent on the scale of the reaction.

In a preferred batch process of the present invention, it is preferred to dissolve the catalyst in the entire amount of alcohol and add the resulting solution to a solution comprising the cosolvent and the source of triglyceride. Stirring and heating may be necessary to dissolve hydroxide catalyst in the alcohol.

In another batch process, a concentrated solution of catalyst in alcohol is prepared and added to a solution

comprising the cosolvent, source of triglyceride, and the remainder of the alcohol. The sodium alkoxide catalyst is preferably prepared by dissolving sodium metal in the alcohol reactant.

In a continuous, industrial process, the cosolvent and excess alcohol are preferably co-distilled at the end of the reaction and then recycled. Therefore, it is preferred to dissolve the catalyst in the cosolvent/alcohol solution and then add this to a reaction vessel containing the source of triglyceride.

Preferably, once the reactants are mixed, stirring is discontinued. Continued stirring may result in the formation of emulsions, particularly when significant amounts of soaps are present.

Once the reaction begins, the reaction mixture immediately becomes cloudy, signifying that glycerol is being produced and is being precipitated from the reaction mixture. Glycerol has a higher density than the alcohol/fatty acid ester/cosolvent phase and therefore forms a glycerol rich lower layer. The lower layer is substantially completely comprised of glycerol, with small amounts of reactants, products and mono- and diglyceride intermediates being present.

The reaction is typically more than about 90% complete after about 20 minutes at a temperature of about 15 to 30°C. The reaction according to the present invention is as much as about 15 times faster than the corresponding reaction without addition of a cosolvent and almost too fast to measure by normal means.

After completion of the reaction, the lower glycerol phase is preferably removed either by drawing it off under gravity or by centrifugation. Gravity separation proceeds about 4 to 5 times more quickly with cosolvent than without, and proceeds substantially without the formation of emulsions. However, centrifugation is quicker than gravity separation. The entire process, including centrifugal

separation of glycerol, may be complete in less than about 20 minutes.

Glycerol is a valuable by-product of the reaction and has many uses such as in resins, pharmaceuticals, soaps, and foods.

After the reaction, the upper layer of the reaction mixture primarily comprises fatty acid esters, excess alcohol and cosolvent. The fatty acid esters typically have much high boiling points than the cosolvent and alcohol and therefore the preferred method of isolation is to distill off the alcohol and cosolvent, leaving behind the esters. The distillation may be carried out either at atmospheric pressure or at reduced pressure. The inventor has found that the heat required for distillation may also assist in driving the reaction to completion.

As discussed above, if hydroxide ion is left in contact with the ester products, the hydroxide may hydrolyze some of the esters to produce soaps. To avoid substantial soap formation, it is preferred that hydroxide ion remaining after the reaction be neutralized by the addition of acid prior to distillation of the cosolvent and excess alcohol.

Because esterification is an equilibrium reaction, it is reasonable to predict that removing the excess methanol before separating the glycerol will result in a reverse transesterification in which glycerol reacts with lower alkyl fatty acid esters to produce fatty acid glycerides. However, the inventor has surprisingly found that the methanol and cosolvent may be co-distilled prior to separation of the glycerol layer without any substantial amount of reverse transesterification. However, the glycerol layer may be removed prior to distillation of the alcohol and cosolvent with equally satisfactory results.

In the most preferred form of the methanolysis reaction, using THF as the cosolvent, the similarity in boiling points of THF and methanol allows a crude form of distillation known as "flashing" to be used to recycle the

cosolvent and excess methanol.

Because the cosolvent is not consumed in the reaction, it is preferably reused a number of times with only a small makeup amount being required for each subsequent reaction.

Prior to using the methyl and ethyl fatty acid esters as fuels, it is preferred that they be purified. Typical purification steps include water washing to remove glycerol, vacuum drying to remove water, and filtration to remove gums and solids which may have been present in the original oil or fat.

It is preferred that the purified esters contain no more than 0.25% total glycerol (including mono- and diglycerides) and no more than 0.03% free glycerol. Glycerol present in the biofuel can clog injectors of diesel engines.

#### Examples

The examples presented below utilize the preferred batch process, adding a solution of catalyst in alcohol to a solution of cosolvent and source of triglyceride. The reactions were conducted at room temperature, used triglyceride sources having an acid value of less than about 1, and were conducted substantially without stirring. A crude ester product was separated. The compositions of the reaction mixture and the crude ester product were analyzed by gas chromatography.

#### Example 1:

To a mixture of soybean oil (100 g, 115 mL) and THF (35 mL) was added dry methanol (28 mL) containing 1.0 g of sodium methoxide (made by adding 0.53 g of sodium metal to methanol). The THF:methanol volumetric ratio was 1.25:1 and the methanol:soybean oil molar ratio was 6:1. After 20 minutes the reaction mixture showed a conversion of 90.1% to the methyl ester. After one hour the lower glycerol layer was gravity-separated. The methanol and THF were flashed

off and a small residual glycerol layer was again gravity separated. The methyl ester layer was washed with 0.5 molar sulfuric acid (1 x 20 mL) and water (2 x 20 mL). The methyl ester layer was dried under vacuum to yield 95 g of crude ester containing more than 95% methyl ester, the remainder being mono- and diglycerides.

Example 2:

To a mixture of soybean oil (100 g, 115 mL) and THF (35 mL) was added dry methanol (28 mL) containing 1.0 g of sodium hydroxide. The THF:methanol volumetric ratio was 1.25:1 and the methanol:soybean oil molar ratio was 6:1. After one minute the reaction mixture showed 68.0% methyl esters, 13.4% monoglycerides, 18.5% diglycerides and 0.47% triglycerides. After 20 minutes the composition was 97.3% methyl esters, 2.5% monoglycerides, 0.2% diglycerides and 0.01% triglycerides. The glycerol layer was gravity-separated. Sulfuric acid (10N, 2.5 mL) was added to neutralize hydroxide ion. The methanol and THF were flashed off, and a small amount of a glycerol/water layer was gravity-separated. The ester layer was washed with water (2 x 25 mL). The methyl ester layer was dried under vacuum to give 90 g of product containing more than 98% methyl esters.

Example 3:

To a mixture of soybean oil (100 g, 115 mL) and 1, 4-dioxane (42 mL) was added dry methanol (28 mL) containing sodium hydroxide (1.0 g). The dioxane:methanol volumetric ratio was 1.5:1 and the methanol:soybean oil molar ratio was 6:1. After one minute the composition of the esters was 87.1% methyl esters, 4.7% monoglycerides, 6.6% diglycerides and 0.96% triglycerides. After 20 minutes the composition comprised 98.6% methyl esters, 1.2% monoglycerides, 0.16% diglycerides and 0.04% triglycerides. The lower glycerol layer was gravity-separated. Sulfuric acid (10N, 2.5 mL) was added. The methanol and dioxane were then flashed off from the methyl ester layer and a small glycerol/water phase

was gravity-separated. The ester layer was washed with water (2 x 25 mL). Vacuum drying gave 90 g of methyl esters containing more than 98% methyl esters, the balance being mono- and diglycerides.

Example 4:

To a mixture of soybean oil (100 g, 115 mL) and THF (10.4 mL) was added dry ethanol (40 mL) containing sodium hydroxide (1.0 g). The volume ratio of THF to ethanol was 0.26:1 and the ethanol:soybean molar ratio was 6:1. After one minute the composition of the esters was 67.9% ethyl esters, 13.4% monoglycerides, 18.5% diglycerides and 0.47% triglycerides. After 20 minutes the composition was 97.3% ethyl esters, 2.5% monoglycerides, 0.2% diglycerides and 0.01% triglycerides. The lower glycerol layer was gravity-separated. The ethanol and THF were then flashed off from the ethyl ester layer. A small glycerol phase was again gravity-separated. The ester layer was washed with 0.5 molar sulfuric acid (1 x 25 mL) and water (2 x 25 mL). Vacuum drying gave 90 g of ethyl ester product, containing more than 98% ethyl esters, the balance being mono- and diglycerides.

Example 5:

To a mixture of coconut oil (100 g, 105 mL) and THF (20.4 mL) was added dry methanol (35.7 mL) containing sodium hydroxide (1.0 g). The THF:methanol volume ratio was 0.57:1 and the methanol:coconut oil molar ratio was 6:1. After one minute the composition of the esters was 89.5% methyl esters, 5.6% monoglycerides, 4.7% diglycerides and 0.14% triglycerides. After 20 minutes the composition was 98.5% methyl esters, 1.2% monoglycerides, 0.3% diglycerides and 0.02% triglycerides. The lower glycerol layer was gravity-separated. Sulfuric acid (10N, 2.5 mL) was added. The methanol and THF were flashed off, and a small glycerol/water layer was gravity-separated. The ester layer was washed with water (2 x 25 mL). Vacuum drying gave 90 g

of methyl ester product, containing more than 98% methyl esters, the balance being mono- and diglycerides.

Example 6:

To a mixture of canola oil (100 g, 115 mL) and THF (36 mL) was added dry methanol (28.8 mL) containing sodium hydroxide (1.0 g). The THF:methanol volume ratio was 1.25:1 and the methanol:canola oil molar ratio was 6:1. After one minute the composition of the esters was 75.5% methyl esters, 9.6% monoglycerides, 13.9% diglycerides and 3.9% triglycerides. After 20 minutes the composition was 95.5% methyl esters, 3.0 monoglycerides, 0.8% diglycerides and 0.6% triglycerides. The lower glycerol layer was gravity-separated. Sulfuric acid (10N, 2.5 mL) was added and then the methanol and THF were flashed off. A small glycerol/water phase was gravity-separated. The ester layer was washed with water (2 x 25 mL). Vacuum drying gave 90.5% methyl ester product containing more than 95% methyl esters, the balance being mono-, di- and triglycerides.

Examples 7 to 15 do not include the step of isolating the crude product. As in Examples 1 to 6, the composition of the reaction mixture is analyzed by gas chromatography. The reaction conditions in Examples 7 to 15 are the same as those in Examples 1 to 6.

Example 7:

To a mixture of soybean oil (20 g, 23 mL) and THF (9.0 mL) was added dry methanol (5.6 mL) containing sodium hydroxide (0.1 g, 0.5% by weight of soybean oil). The THF:methanol volume ratio was 1.6:1 and the methanol:soybean oil molar ratio was 6:1. After one minute the composition of the esters was 69.3% methyl esters, 8.2% monoglycerides, 15.4% diglycerides and 7.2% triglycerides. After 20 minutes the composition was 86.3% methyl esters, 4.9% monoglycerides, 2.7% diglycerides and 6.1% triglycerides.

**Example 8:**

To a mixture of soybean oil (20 g, 23 mL) and THF (9.0 mL) was added dry methanol (5.6 mL) containing sodium hydroxide (0.2 g, 1% by weight of soybean oil). The THF:methanol volume ratio was 1.6:1 and the methanol:soybean oil molar ratio was 6:1. After one minute the composition of the esters was 75.2% methyl esters, 7.6% monoglycerides, 13.4% diglycerides and 3.7% triglycerides. After 20 minutes the composition was 94.4% methyl esters, 4.4% monoglycerides and 1.2% diglycerides.

**Example 9:**

To a mixture of soybean oil (20 g, 23 mL) and THF (9.0 mL) was added dry methanol (5.6 mL) containing sodium hydroxide (0.4 g, 2% by weight of soybean oil). After one minute the composition of the esters was 89.8% methyl esters, 4.5% monoglycerides, 3.8% diglycerides and 1.9% triglycerides. After 20 minutes the composition was 98.9% methyl esters, 1.0% monoglycerides, 0.1% diglycerides and 0.04% triglycerides.

**Example 10:**

To a mixture of canola oil (19.5 g, 22.4 mL) and THF (9.0 mL) was added dry methanol (5.6 mL) containing sodium hydroxide (0.1 g, 0.5% by weight of canola oil). The THF:methanol volume ratio was 1.6:1 and the methanol:canola oil molar ratio was 6:1. After one minute the composition of the esters was 65.1% methyl esters, 10.6% monoglycerides, 17.1% diglycerides and 7.1% triglycerides. After 20 minutes the composition was 74.2% methyl esters, 9.1% monoglycerides, 7.9% diglycerides and 8.7% triglycerides.

**Example 11:**

To a mixture of canola oil (19.5 g, 22.4 mL) and THF (9.0 mL) was added dry methanol (5.6 mL) containing sodium hydroxide (0.2 g, 1.0% by weight of canola oil). The

THF:methanol volume ratio was 1.6:1 and the methanol:canola oil molar ratio was 6:1. After one minute the composition of the esters was 72.5% methyl esters, 9.6% monoglycerides, 13.9% diglycerides and 3.9% triglycerides. After 20 minutes the composition was 95.6% methyl esters, 3.0% monoglycerides, 0.8% diglycerides and 0.6% triglycerides.

Example 12:

To a mixture of canola oil (19.5 g, 22.4 mL) and THF (9.0 mL) was added dry methanol (5.6 mL) containing sodium hydroxide (0.4 g, 2% by weight of canola oil). The THF:methanol volume ratio was 1.6:1 and the methanol:canola oil molar ratio was 6:1. After one minute the composition of the esters was 97.4% methyl esters, 1.9% monoglycerides, 0.6% diglycerides and 0.1% triglycerides. After 20 minutes the composition was 98.7% methyl esters, 1.1% monoglycerides, 0.1% diglycerides and 0.1% triglycerides.

Example 13:

To a mixture of soybean oil (20 g, 23 mL) and 1,4-dioxane (10.8 mL) was added dry methanol (5.6 mL) containing sodium hydroxide (0.2 g, 1% by weight of soybean oil). The dioxane:methanol volume ratio was 1.9:1 and the methanol:soybean oil molar ratio was 6:1. After one minute the composition of the esters was 87.1% methyl esters, 4.7% monoglycerides, 6.6% diglycerides and 1.0% triglycerides. After 20 minutes the composition was 98.7% methyl esters, 1.2% monoglycerides, 0.2% diglycerides and 0.04% triglycerides.

Example 14:

To a mixture of soybean oil (20 g, 23 mL) and THF (2.6 mL) was added dry ethanol (8.0 mL) containing sodium hydroxide (0.2 g, 1% by weight of soybean oil). The THF:ethanol volume ratio was 0.3:1 and the ethanol:soybean oil molar ratio was 6:1. After one minute the composition

of the esters was 68.0% ethyl esters, 13.4% monoglycerides, 18.5% diglycerides and 0.5% triglycerides. After 20 minutes the composition was 97.3% ethyl esters, 2.5% monoglycerides, 0.2% diglycerides and 0.01% triglycerides.

Example 15:

To a mixture of coconut oil (15.7 g, 16.5 mL) and THF (4.0 mL) was added dry methanol (5.6 mL) containing sodium hydroxide (0.2 g, 1.0% by weight of coconut oil). The THF:methanol volume ratio was 0.7:1 and the methanol:coconut oil molar ratio was 6:1. After one minute the composition of the esters was 89.5% methyl esters, 5.6% monoglycerides, 2.7% diglycerides and 2.2% triglycerides. After 20 minutes the composition was 98.5% methyl esters, 0.9% monoglycerides, 0.6% diglycerides and 0.01% triglycerides.

Although the invention has been described in connection with certain preferred embodiments, it is not intended to be limited thereto. Rather, it is intended that the invention cover all alternate embodiments as may be within the scope of the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the production of lower alkyl esters of fatty acids, comprising:

reacting a source of fatty acid glycerides with an alcohol in the presence of an esterification catalyst and a cosolvent, wherein:

(a) the source of fatty acid glycerides is selected from the group comprising fats and oils derived from plants and animals;

(b) the alcohol is selected from the group comprising methanol, ethanol and mixtures thereof in an amount sufficient to substantially completely convert the source of fatty acid glycerides to lower alkyl fatty acid monoesters;

(c) the esterification catalyst is present in an amount sufficient to catalyze the process; and

(d) the cosolvent is present in at least an amount sufficient to solubilize the source of fatty acid glycerides in the alcohol at a temperature below the boiling point of the alcohol;

the process being carried out at a temperature below the boiling point of the alcohol for a time sufficient to allow the source of fatty acids to be substantially completely converted to lower alkyl fatty acid esters; and

after completion of the reaction, separating the lower alkyl fatty acid esters from the reaction mixture.

2. The process of claim 1, wherein the cosolvent is a cyclic ether selected from the group comprising tetrahydrofuran and 1,4-dioxane.

3. The process of claim 2, wherein the cosolvent is tetrahydrofuran.

4. The process of claim 2, wherein the cosolvent is tetrahydrofuran and the alcohol is methanol.
5. The process of claim 1, wherein the catalyst is selected from the group comprising hydroxides and alkoxides.
6. The process of claim 5, wherein the catalyst is a hydroxide selected from the group comprising sodium hydroxide and potassium hydroxide.
7. The process of claim 5, wherein the catalyst is sodium methoxide.
8. The process of claim 1, wherein the alcohol is methanol and the reaction is conducted at a temperature below about 65°C.
9. The process of claim 8, wherein the temperature is in the range of about 15°C to about 30°C.
10. The process of claim 1, wherein the source of fatty acid glycerides is selected from the group comprising beef tallow, coconut oil, corn oil, cottonseed oil, lard, olive oil, palm oil, palm kernel oil, peanut oil, soybean oil, linseed oil, tung oil, sunflower oil, safflower oil, canola oil, sesame oil, babassu oil, perilla oil, oiticica oil, fish oils, menhaden oil, castor oil, rapeseed oil, Chinese tallow tree oil, Physic nut oil, Cuphea seed oil, microalgal oils, bacterial oils and fungal oils.
11. The process of claim 10, wherein the source of fatty acid glycerides is selected from the group comprising soybean oil, palm oil, palm kernel oil, coconut oil and canola oil.
12. The process of claim 1, wherein the alcohol is ethanol and the reaction is conducted at a temperature below

about 78°C.

13. The process of claim 1, wherein the source of fatty acid glycerides has an acid value of less than about 1.

14. A process for the production of methyl esters of fatty acids, comprising reacting a source of fatty acid glycerides with an alcohol in the presence of an esterification catalyst and a cosolvent wherein:

(a) the source of fatty acid glycerides is selected from the group comprising fats and oils derived from animals and plants having an acid value less than about 1;

(b) the alcohol is methanol in a molar ratio of about 6:1 to the source of fatty acid glycerides;

(c) the catalyst is selected from the group comprising sodium methoxide and sodium hydroxide and is present in an amount of about 0.4 to 2% by weight of fatty acid glyceride; and

(d) the cosolvent is tetrahydrofuran and is present in at least an amount sufficient to solubilize the source of fatty acid glycerides in methanol;

the process being carried out at about 15 to 30°C and reacted without agitation for a time sufficient to allow the source of fatty acid glycerides to be substantially completely converted to methyl esters of fatty acids; and

separating the methyl fatty acid esters from the reaction mixture.

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